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(54) **Fluoroelastomer compositions**

(57) Fluoropolymers comprising a fluoroelastomer matrix incorporating therein particles of a semicrystalline fluoropolymer containing iodine and/or bromine and formed of tetrafluoroethylene (TFE) homopolymers or copolymers wherein the average particle sizes of the semicrystalline fluoropolymer latex range from 10 to 100 nm.

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Description

[0001] The present invention relates to fluoropolymers essentially formed of a mixture of a fluoroelastomer and a semicrystalline fluoropolymer having improved mechanical properties and usable for sealing manufactured articles in the electronic, optical and pharmaceutical industry.

[0002] More specifically the present invention relates to fluoropolymers formed of a mixture of a fluoroelastomer and a semicrystalline fluoropolymer containing iodine and/or bromine, characterized by improved mechanical properties combined with good properties of elastic retention (lower compression set) and very good surface appearance without roughness. It is well known that one of the fluoroelastomer uses is the preparation of O-rings for seals: for this application it is essential that the O-ring surface is smooth.

[0003] The use of fluoroelastomers containing polytetrafluoroethylene (PTFE) particles to improve the properties of abrasion-resistance and of hot tearing of the obtained manufactured articles is known in the prior art. As described in Japanese patent 57-107,336, the fluoroelastomer abrasion-resistance is improved by physically mixing solid curable fluoroelastomers with PTFE powders having a low molecular weight, in the range 500-200,000 as average molecular weight by number (M_n). Said PTFE is prepared by thermal decomposition at a temperature between 450°C and 600°C for prolonged times or by irradiation with ionic radiation of high molecular weight PTFE. An alternative method for obtaining PTFE having a low molecular weight is that to polymerize TFE in the presence of chain transfer agents. The fluoroelastomer and the PTFE powders are mixed in Banbury or in calender.

[0004] In USP 4,879,362 and USP 4,904,726 mixtures of fluoroelastomers with resins of PTFE modified with the addition of comonomers such as hexafluoropropene (HFP), perfluoropropylvinylether (PPVE), etc., are used, in order to avoid PTFE fibrillation problems without losing the reinforcement properties that the PTFE gives to the obtained fluoroelastomers. The comonomer results much more present on the polymer particle surface, so as to allow an uniform distribution in the fluoroelastomer without the formation of visible agglomerates. These latter should be the cause of fibrillation phenomena.

[0005] In EP 708,797 fluoroelastomer compositions formed of a fluoroelastomer and by a semicrystalline fluorinated filler in the form of micropowder which are obtained in curing compounds not containing metal species, are described. Said compositions give a low release of metal species under conditions where an high purity is required, but they show poor mechanical properties. Tests carried out by the Applicant (see the comparative Examples), have shown that the surface of the manufactured articles obtained from said fluoroelastomer compositions shows roughness. It is well known that in the O-ring preparation, typical fluoroelastomer application, surfaces having a low roughness in order to obtain good sealing properties, are required. The semicrystalline fluorinated filler is based on PTFE or PTFE modified with a comonomer and obtained by emulsion or suspension polymerization. The high molecular weight PTFE is subjected to irradiation, as above said, in order to reduce the molecular weight. This makes easier the PTFE milling produced by a suspension process; it eliminates the fibrillation and reduces the PTFE agglomeration obtained by an emulsion process.

[0006] The need was felt to have available fluoroelastomer compositions comprising a semicrystalline fluorinated filler having improved properties compared with those of the prior art and specifically with the following property combination:

- improved mechanical properties
- good elastic retention properties (lower compression set-very good seal)
- very good surface appearance roughness free.

[0007] The Applicant has unexpectedly and surprisingly found that it is possible to obtain the combination of the above mentioned properties, by incorporating in the fluoroelastomer matrix PTFE particles or its copolymers having well defined sizes as specified hereinafter.

[0008] It is therefore an object of the present invention fluoropolymers comprising a fluoroelastomer matrix incorporating therein particles of a semicrystalline fluoropolymer latex containing iodine and/or bromine and formed of tetrafluoroethylene (TFE) homopolymers, or TFE copolymers with one or more monomers containing at least one ethylene unsaturation in amounts ranging from 0.01% to 10% by moles, preferably from 0.05% to 5% by moles, wherein the average particle sizes of the semicrystalline fluoropolymer latex range from 10 to 100 nm, preferably from 10 to 60 nm. Also semicrystalline fluoropolymers wherein the latex particle sizes have the above mentioned value for at least 60% by weight, preferably 70% by weight of the semicrystalline fluoropolymer, can be used. The invention compositions are obtainable by mixing the semicrystalline fluoropolymer latex containing iodine and/or bromine with the fluoroelastomer latex and subsequent coagulation. Alternatively the invention compositions can be polymerized in the same reactor in two subsequent steps: in a first step the semicrystalline fluoropolymer with the mentioned nanometric sizes and containing iodine is polymerized and in a second step the fluoroelastomer is polymerized. By operating in this way the fluoroelastomer should cover the semicrystalline fluoropolymer latex particles, allowing to obtain a very good dispersion

of the latter in the fluoroelastomer.

[0009] The semicrystalline fluoropolymer amount inside the fluoroelastomer matrix is in the range 2%-40% by weight, preferably 5-30% by weight, more preferably 10-20% by weight on the total of the polymer mixture.

[0010] The semicrystalline fluoropolymer particles having the above mentioned sizes are obtainable for example by a polymerization process in an aqueous microemulsion of perfluoropolyoxyalkylenes as described for example in the European patent application EP 991 12083.3 in the name of the Applicant, herein incorporated by reference. Microemulsion polymerization methods can also be used, wherein the oil phase is formed of polymerizable unsaturated monomers, as described in USP 5,523,346 and in USP 5,616,648.

[0011] The semicrystalline fluoropolymers of the present invention contain in the end group of the macromolecules and/or in the chain iodine and/or bromine atoms. The introduction of said iodine and/or bromine atoms can be carried out by addition, in the reaction mixture, of brominated and/or iodinated comonomers as described for example in USP 4,035,565, USP 4,694,045, USP 4,745,165, USP 4,564,662 and EP 199,138, in such amounts wherefore the comonomer content in the final product is generally in the range 0.05-2 moles for 100 moles of the other base monomer units.

[0012] Alternatively or also in association with these comonomers, it is possible to introduce iodine and/or bromine end atoms by addition to the reaction mixture of iodinated and/or brominated chain transfer agents (see for example USP 4,243,770 and USP 4,943,622, USP 5,173,553) in such amounts whereby the iodine content by weight in the semicrystalline fluoropolymer is in the range 0.01-5%, preferably 0.05-1% by weight.

[0013] The brominated and iodinated compounds are those mentioned hereinunder in the fluoroelastomer preparation.

[0014] The fluoroelastomers can be prepared by copolymerization of the monomers in aqueous emulsion, according to well known methods in the prior art, in the presence of radical initiators (for example alkaline or ammonium persulphates, perphosphates, perborates or percarbonates), optionally in combination with ferrous, cuprous or silver salts, or of other easily oxidizable metals. In the reaction medium also surfactants of various kind, among which the fluorinated surfactants are particularly preferred, are usually present.

[0015] Alternatively the fluoroelastomers can be prepared in bulk or in suspension, in an organic liquid in which a suitable radical initiator is present, according to well known techniques.

[0016] The polymerization reaction is generally carried out at temperatures in the range 25°-150°C, under a pressure up to 10 MPa.

[0017] The fluoroelastomers are preferably prepared in microemulsion of perfluoropolyoxyalkylenes, according to USP 4,789,717 and USP 4,864,006.

[0018] The Applicant has found that in order to obtain the results of the present invention it is essential that the latex of the semicrystalline fluoropolymer filler has the mentioned nanometric sizes, while the size of the latex of the fluoroelastomer is not critical.

[0019] When the semi-crystalline fluorinated filler is based on modified PTFE, for its preparation comonomers having an ethylene unsaturation both of hydrogenated and fluorinated type, can be used. Among those hydrogenated, ethylene, propylene, acrylic monomers, for example methylmethacrylate, (meth)acrylic acid, butylacrylate, hydroxyethylhexyl-acrylate, styrene monomers can be mentioned.

[0020] Among the fluorinated comonomers we can mention:

- perfluoroolefins C_3-C_8 , such as hexafluoropropene (HFP), hexafluoroisobutene;
- hydrogenated fluoroolefins C_2-C_8 , such as vinyl fluoride (VF), vinylidene fluoride (VDF), trifluoroethylene, perfluoroalkylethylene $CH_2=CH-R_f$, wherein R_f is a perfluoroalkyl C_1-C_6 ;
- chloro- and/or bromo- and/or iodo-fluoroolefins C_2-C_8 , such as chlorotrifluoroethylene (CTFE);
- (per)fluoroalkylvinylethers (PAVE) $CF_2=CFOR_f$, wherein R_f is a (per)fluoroalkyl C_1-C_6 , for example CF_3 , C_2F_5 , C_3F_7 ;
- (per)fluoro-oxyalkylvinylethers $CF_2=CFOX$, wherein X is: an alkyl C_1-C_{12} , or an oxyalkyl C_1-C_{12} , or a (per)fluoroalkoxyalkyl C_1-C_{12} having one or more ether groups, for example perfluoro-2-propoxy-propyl; fluorodioxoles, preferably perfluorodioxoles.

[0021] PAVES are preferred comonomers, specifically perfluoromethyl-, ethyl-, propylvinylether and fluorodioxoles, preferably perfluorodioxoles.

[0022] The fluoroelastomers used in the present invention belong to the following classes:

- (1) VDF-based copolymers, wherein VDF is copolymerized with at least one comonomer selected from the following: perfluoroolefins C_2-C_8 , such as tetrafluoroethylene (TFE), hexafluoropropene (HFP); chloro- and/or bromo- and/or iodo-fluoroolefins C_2-C_8 , such as chlorotrifluoroethylene (CTFE) and bromotrifluoroethylene; (per)fluoroalkylvinylethers (PAVE) $CF_2=CFOR_f$, wherein R_f is a (per)fluoroalkyl C_1-C_6 , for example trifluoromethyl, bromodifluoromethyl, pentafluoropropyl; perfluoroalkoxyalkylvinylethers $CF_2=CFOX$, wherein X is a perfluoro-oxyalkyl C_1-C_{12}

having one or more ether groups, for example perfluoro-2-propoxy-propyl; non fluorinated olefins (OI) C₂-C₈, for example ethylene and propylene;

(2) TPE-based copolymers, wherein TFE is copolymerized with at least one comonomer selected from the following: (per)fluoroalkylvinylethers (PAVE) CF₂=CFOR_f, wherein R_f is as above defined; perfluoro-oxyalkylvinylethers CF₂=CFOX, wherein X is as above defined; fluoroolefins C₂-C₈ containing hydrogen and/or chlorine and/or bromine and/or iodine atoms; non fluorinated olefins (OI) C₂-C₈; perfluorovinylethers containing hydrocyanic groups as described in USP 4,281,092, USP 5,447,993, USP 5,789,489.

[0023] Preferably the invention fluoroelastomers contain per-fluorinated monomers, and preferably the base structure of these fluoroelastomers is selected from the copolymers of class (2), wherein TFE is polymerized with one or more perfluorinated comonomers as above mentioned.

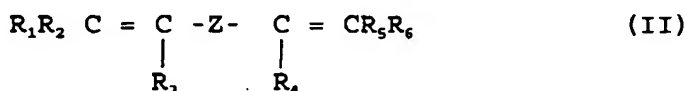
[0024] Within the above defined classes, preferred compositions by moles of the monomers forming the fluoroelastomer base structure are the following:

- (a) vinylidene fluoride (VDF) 45-85%, hexa-fluoropropene (HFP) 15-45%, tetrafluoroethylene (TFE) 0-30%;
- (b) vinylidene fluoride (VDF) 50-80%, perfluoroalkylvinylether (PAVE) 5-50%, tetrafluoroethylene (TFE) 0-20%;
- (c) vinylidene fluoride (VDF) 20-30%, non fluorinated olefins (OI) C₂-C₈ 10-30%, hexafluoropropene (HFP) and/or perfluoroalkylvinylether (PAVE) 18-27%, tetrafluoroethylene (TFE) 10-30%;
- (d) tetrafluoroethylene (TFE) 50-80%, perfluoroalkylvinylether (PAVE) 20-50%;
- (e) tetrafluoroethylene (TFE) 45-65%, non fluorinated olefins (OI) C₂-C₈ 20-55%, vinylidene fluoride 0-30%;
- (f) tetrafluoroethylene (TFE) 32-60% by moles, non fluorinated olefins (OI) C₂-C₈ 10-40%, perfluoroalkylvinylether (PAVE) 20-40%;
- (g) tetrafluoroethylene (TFE) 33-75%, perfluoroalkylvinylether (PAVE) 15-45%, vinylidene fluoride (VDF) 5-30%.

[0025] Particularly preferred specific compositions are:

- (d) TFE 50-80%, PAVE 20-50%;
- (g) TFE 33-75%, PAVE 15-45%, VDF 5-30%.

[0026] Optionally the fluoroelastomers comprise also monomer units deriving from a bis-olefin having general formula:



wherein:

R₁, R₂, R₃, R₄, R₅, R₆, equal to or different from each other, are H or alkyls C₁-C₅;
Z is a linear or branched, alkylene or cycloalkylene C₁-C₁₈ radical, optionally containing oxygen atoms, preferably at least partially fluorinated, or a (per)fluoropolyoxyalkylene radical, as described in EP 661,304 in the name of the Applicant.

[0027] The unit amount in the chain deriving from said bis-olefins is generally in the range 0.01-1.0 by moles, preferably 0.03-0.5 by moles, still more preferably 0.05-0.2% by moles for 100 moles of the other above mentioned monomer units forming the fluoroelastomer base structure.

[0028] The fluoropolymers of the present invention can be cured by peroxidic route, wherefore they preferably contain along the chain and/or in the end position of the macromolecules iodine and/or bromine atoms. The introduction of said iodine and/or bromine atoms can be achieved by addition, in the reaction mixture, of brominated and/or iodinated cure-site comonomers, such as bromine and/or iodine olefins having from 2 to 10 carbon atoms (as described for example in USP 4,035,565 and USP 4,694,045), or iodo and/or bromo fluoroalkylvinylethers (as described in USP 4,745,165, USP 4,564,662 and EP 199,138), in such amounts so that the content of cure-site comonomer in the final product is generally in the range 0.05-2 moles for 100 moles of the other base monomer units.

[0029] Other usable iodinated compounds are the triiodinated ones deriving from triazines as described in European patent application EP 860,436 and in the European patent application EP 99114823.0.

[0030] Alternatively or also in association with the cure-site comonomers it is possible to introduce iodine and/or

bromine end atoms by addition to the reaction mixture of iodinated and/or brominated chain transfer agents, such as for example the compounds of formula $R_1(I)_x(Br)_y$, wherein R_1 is a (per)fluoroalkyl or a (per)fluorochloroalkyl having from 1 to 8 carbon atoms, while x and y are integers between 0 and 2, with $1 \leq x+y \leq 2$ (see for example USP 4,243,770 and USP 4,943,622). It is also possible to use, as chain transfer agents, alkaline or earth-alkaline metal iodides and/or bromides, according to USP 5,173,553.

[0031] In association with the chain transfer agents containing iodine and/or bromine, other chain transfer agents known in the prior art, such as ethyl acetate, diethylmalonate, etc., can be used.

[0032] Curing by peroxidic route is carried out, according to known techniques, by addition of a suitable peroxide capable to generate radicals by thermal decomposition. Among the most commonly used we can mention: dialkylperoxides, such as for example di-terbutyl-peroxide and 2,5-dimethyl-2,5-di-(terbutylperoxy)hexane; dicumyl peroxide; dibenzoyl peroxide; di-terbutyl perbenzoate; di [1,3-dimethyl-3-(terbutyl-peroxy)butyl]carbonate. Other peroxidic systems are described, for example, in European patent applications EP 136,596 and EP 410,351.

[0033] To the compound (curable blend) other products are then added, such as:

(a) curing coagents, in amounts generally in the range 0.5-10%, preferably 1-7% by weight with respect to the polymer; among them, triallyl-cyanurate; triallyl-isocyanurate (TAIC); tris(diallylamine)-s-triazine; triallylphosphite; N,N-diallyl-acrylamide; N,N,N',N'-tetraallylmalonamide; trivinyl-isocyanurate; 2,4,6-trivinyl-methyltrisiloxane, etc., are commonly used; TAIC is particularly preferred; other preferred crosslinking agents are bis-olefins described in the European patent application EP 769,520.

Other crosslinking agents which can be used are the triazines described in the European patent application EP 860,436 and in the patent WO97/05122.

(b) optionally a metal compound, in amounts in the range 1-15%, preferably 2-10%, by weight with respect to the polymer, selected from oxides or hydroxides of divalent metals, such as for example, Mg, Zn, Ca or Pb, optionally associated to a weak acid salt, such as for example stearates, benzoates, carbonates, oxalates or phosphites of Ba, Na, K, Pb, Ca;

(c) optionally acid acceptors of the non metal oxide type, such as 1,8 bis dimethyl amino naphthalene, octadecylamine etc. as described in EP 708,797.

(d) other conventional additives, such as thickening fillers, pigments, antioxidants, stabilizers and the like.

[0034] When the fluoroelastomer matrix contains cyano groups, the fluoropolymer curing of the present invention is carried out by using as crosslinking agents tin organic compounds or di-aromatic aminic compounds, as described in USP 4,394,489, USP 5,767,204, USP 5,789,509. This kind of curing can be associated to a curing of peroxidic type, when the fluoroelastomer matrix contains iodine and/or bromine atoms, preferably end atoms, as described in USP 5,447,993.

[0035] The present invention will be now better illustrated by the following Examples, which have a merely indicative but not limitative purpose of the scope of the invention itself.

EXAMPLE 1

a) Preparation of the semicrystalline fluoropolymer

[0036] In a 10 l autoclave, equipped with a stirrer working at 545 rpm, after evacuation, 6.5 l of demineralized water and 260 ml of a perfluoropolyoxyalkylene microemulsion were introduced: the latter was previously obtained by mixing:

- 56.4 ml of a perfluoropolyoxyalkylene having an acid end group of formula:



wherein $n/m = 10$, having average molecular weight of 600;

- 56.4 ml of a 30% by volume NH_4OH aqueous solution;
- 112.8 ml of demineralized water;
- 34.4 ml of Galden^(R) D02 of formula:



wherein $n/m = 20$, having average molecular weight of 450.

[0037] The autoclave was then heated up to 80°C and maintained at said temperature for the whole reaction dura-

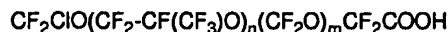
tion. 0.48 bar of C_2H_6 were fed into the autoclave and the pressure was increased and maintained constant at 25 bar during the whole polymerization with TFE.

[0038] 1.3 g of ammonium persulphate (APS) as initiator agent and at 66% of the monomer conversion 3 g of iodinated transfer agent $C_6F_{12}I_2$ were then introduced into the autoclave. After 27 minutes of reaction, the autoclave was cooled and the latex discharged. The latex characteristics are reported in Table 1.

b) Preparation of the fluoroelastomer

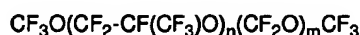
[0039] In a 10 l autoclave, equipped with a stirrer working at 545 rpm, after evacuation, 6.5 l of demineralized water and 67 ml of a perfluoropolyoxyalkylene microemulsion were introduced: the latter was previously obtained by mixing:

- 14.5 ml of a perfluoropolyoxyalkylene having an acid end group of formula:



wherein $n/m = 10$, having average molecular weight of 600;

- 14.5 ml of a 30% by volume NH_4OH aqueous solution;
- 29 ml of demineralized water;
- 9 ml of Galden^(R) D02 of formula:



wherein $n/m = 20$, having average molecular weight of 450.

[0040] The autoclave was then heated up to 80°C and maintained at said temperature for the whole reaction duration. The following mixture of monomers was then fed:

perfluoromethylvinylether (PMVE)

60% by moles

tetrafluoroethylene (TFE)

40% by moles

so as to increase the pressure to 25 bar.

- 0.32 g of ammonium persulphate (APS) as initiator agent;
- 26 g of 1,6-diiodoperfluorohexane ($C_6F_{12}I_2$) as chain transfer agent;
- 5 g of bis-olefin of formula $CH_2=CH-(CF_2)_6-CH=CH_2$; the addition was carried out in 20 portions, each of 0.25 g, starting from the polymerization beginning and for every 5% increase in the monomer conversion, were then introduced in the autoclave.

[0041] The 25 bar pressure was maintained constant for the whole duration of the polymerization by feeding a mixture formed of:

perfluoromethylvinylether (PMVE)

40% by moles

tetrafluoroethylene (TFE)

60% by moles

[0042] After 137 minutes of reaction, the autoclave was cooled and the latex discharged. The latex properties are reported in Table 1.

c) Mixing of the latexes - Preparation of the final polymer

[0043] 595 ml of the latex obtained in Example 1a are mixed with 1518 ml of the Example 1b latex. After mixing, the latex is coagulated with an aluminum sulphate solution (6 g of $Al_2(SO_4)_3$ for each litre of latex) and dried at 80°C in an air-circulating oven for 10 hours. 500 g of polymer, characterized as shown in Table 2, were obtained.

EXAMPLE 1D (comparative)

- [0044] 425 g of fluoroelastomer obtained in Example 1b were mechanically mixed with 75 g of PTFE MP 1600 by Du Pont in an open mixer with the rollers heated at 60°C. In the mixing process the perfluoroelastomer is introduced first with the rollers completely close and mixed until a continuous polymer film is obtained. The PTFE powder was then added until an uniform mixing was obtained. The obtained mixture has been characterized as reported in Table 2.

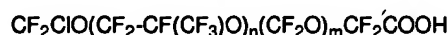
EXAMPLE 2

- [0045] The polymer obtained in Example 1c was crosslinked with bis-olefin of formula $\text{CH}_2=\text{CH}-(\text{CF}_2)_6-\text{CH}=\text{CH}_2$, instead of triallylisocyanurate (TAIC). The compound characteristics are reported in Table 2 together with the thermal resistance properties at 290°C which confirm the resistance characteristics at high temperatures obtained by using the bis-olefin as crosslinking agent in the peroxidic curing.

EXAMPLE 3

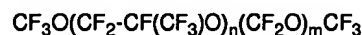
- [0046] In a 10 l autoclave, equipped with a stirrer working at 545 rpm, after evacuation, 6.5 l of demineralized water and 260 ml of a perfluoropolyoxyalkylene microemulsion were introduced: the latter was previously obtained by mixing:

- 56.3 ml of a perfluoropolyoxyalkylene, having an acid end group, of formula:



wherein $n/m = 10$, having average molecular weight of 600;

- 56.3 ml of a 30% by volume NH_4OH aqueous solution;
- 112.7 ml of demineralized water;
- 34.7 ml of Galden^(R) D02 of formula:



wherein $n/m = 20$, having average molecular weight of 450.

- [0047] The autoclave was then heated up to 80°C and maintained at said temperature for the whole reaction duration. 0.48 bar of ethane were fed into the autoclave and the pressure was increased and maintained constant at 25 bar by continuously feeding TFE during the polymerization.

- [0048] 1.3 g of ammonium persulphate (APS) as initiator agent and at 66% of the monomer conversion 3 g of $\text{C}_6\text{F}_{12}\text{I}_2$ as chain transfer agent were then introduced into the autoclave.

- [0049] After 30 minutes of reaction, the autoclave was cooled, degassed and discharged. The latex characteristics are reported in Table 1. Subsequently 5059.5 ml (corresponding to 637.5 g of polymer) of the latex are introduced again in the 10 litre reactor to which 1440 ml of demineralized water are added. The autoclave is then heated up to 90°C and maintained for one hour at said temperature in order to decompose all the residual initiator agent. Subsequently the temperature is increased up to 80°C and maintained constant for the whole duration of the polymerization. The following mixture of monomers was then fed:

perfluoromethylvinylether (PMVE)

60% by moles

- tetrafluoroethylene (TFE)

40% by moles

so as to increase the pressure to 25 bar.

- 0.32 g of ammonium persulphate (APS) as initiator agent;
- 22.3 g of 1,6-diiodoperfluorohexane ($\text{C}_6\text{F}_{12}\text{I}_2$) as chain transfer agent;
- 4.28 g of bis-olefin of formula $\text{CH}_2=\text{CH}-(\text{CF}_2)_6-\text{CH}=\text{CH}_2$; the addition was carried out in 20 portions, each of 0.214 g, starting from the polymerization beginning and for every 5% increase in the monomer conversion,

were then introduced in the autoclave.

[0050] The 25 bar pressure was maintained constant for the whole duration of the polymerization by feeding a mixture formed of:

perfluoromethylvinylether (PMVE)
40% by moles

tetrafluoroethylene (TFE)

60% by moles

[0051] After 230 minutes of reaction corresponding to 2550 g of elastomer, the autoclave was cooled and the latex discharged. The latex is coagulated with an aluminum sulphate solution (6 g of $Al_2(SO_4)_3$ for each litre of latex) and dried at 80°C in an air-circulating oven for 10 hours. The obtained polymer was characterized as shown in Table 2.

EXAMPLE 4

a) Preparation of the semicrystalline fluoropolymer

[0052] In a 10 l autoclave, equipped with a stirrer working at 545 rpm, after evacuation, 6.5 l of demineralized water and 65.1 ml of a perfluoropolyoxyalkylene microemulsion were introduced: the latter was previously obtained by mixing:

- 14.1 ml of a perfluoropolyoxyalkylene, having an acid end group, of formula:



wherein $n/m = 10$, having average molecular weight of 600;

- 14.1 ml of a 30% by volume NH_4OH aqueous solution;
- 28.2 ml of demineralized water;
- 8.7 ml of Galden^(R) D02 of formula:



wherein $n/m = 20$, having average molecular weight of 450.

[0053] The autoclave was then heated up to 80°C and maintained at said temperature for the whole reaction duration. The autoclave was pressurized to the pressure of 0.56 bar with ethane and then to the pressure of 25 bar with a monomer mixture formed of 10% by moles of perfluoromethylvinylether (PMVE) and 90% by moles of tetrafluoroethylene (TFE).

[0054] In the autoclave 1.3 g of ammonium persulphate (APS) as initiator agent were then introduced. During the reaction the pressure is maintained at 25 bar by continuously feeding the following monomer mixture: 3.5% by moles of PMVE and 96.5% of TFE.

[0055] After 60 minutes of reaction, the autoclave was cooled. Subsequently the latex was heated at 95°C for 45 minutes in order to eliminate the residual APS. The temperature has then been decreased again to 80°C and maintained constant for the whole duration of the polymerization. The following mixture of monomers was then fed:

TFE 90% by moles
MVE 10% by moles

so as to increase the pressure to 25 bar. In the autoclave

- 1.3 g of APS
- 0.27 g of $C_6F_{12}I_2$.

were then introduced.

[0056] The 25 bar pressure was maintained constant for the whole duration of the polymerization by feeding a mixture formed of:

TFE 96.5% by moles

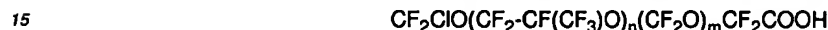
MVE 3.5% by moles

5 [0057] After 5 minutes of reaction, corresponding to 250 g of polymer produced, the autoclave was cooled and the latex discharged. The latex properties are reported in Table 3.

b) Preparation of the fluoroelastomer

10 [0058] In a 22 l autoclave, equipped with a stirrer working at 460 rpm, after evacuation, 15 l of demineralized water and 154.5 ml of a perfluoropolyoxyalkylene microemulsion were introduced: the latter was previously obtained by mixing:

- 33.46 ml of a perfluoropolyoxyalkylene, having an acid end group, of formula:



wherein $n/m = 10$, having average molecular weight of 600;

- 33.46 ml of a 30% by volume NH_4OH aqueous solution;
- 66.93 ml of demineralized water;
- 20 - 20.65 ml of Galden^(R) D02 of formula:



wherein $n/m = 20$, having average molecular weight of 450.

25 [0059] The autoclave was then heated up to 80°C and maintained at said temperature for the whole reaction duration. The following mixture of monomers was then fed:

perfluoromethylvinylether (PMVE)

30 60% by moles

tetrafluoroethylene (TFE)

40% by moles

so as to increase the pressure to 25 bar.

- 35
- 0.75 g of ammonium persulphate (APS) as initiator agent;
 - 69.24 g of 1,6-diiodoperfluorohexane ($\text{C}_6\text{F}_{12}\text{I}_2$) as chain transfer agent;
 - 11.09 g of bis-olefin of formula $\text{CH}_2=\text{CH}(\text{CF}_2)_6\text{CH}=\text{CH}_2$; the addition was effected in 20 portions, each of 0.554 g, starting from the polymerization beginning and for every 5% increase in the monomer conversion,
 - 40 were then introduced in the autoclave.

[0060] The 25 bar pressure was maintained constant for the whole duration of the polymerization by feeding a mixture formed of:

45 perfluoromethylvinylether (PMVE)

40% by moles

tetrafluoroethylene (TFE)

60% by moles

50 [0061] After 110 minutes of reaction, the autoclave was cooled and the latex discharged. The latex properties are reported in Table 3.

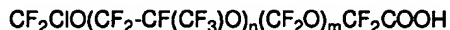
c) Mixing of the latexes - Preparation of the final polymer

55 [0062] 382.6 ml of the latex obtained in Example 4a are mixed with 1187 ml of the Example 4b latex. After mixing, the latex is coagulated with an aluminum sulphate solution (6 g of $\text{Al}_2(\text{SO}_4)_3$ for each litre of latex) and dried at 80°C in an air-circulating oven for 10 hours. 500 g of polymer, characterized as shown in Table 4, were obtained.

EXAMPLE 5

[0063] In a 10 l autoclave, equipped with a stirrer working at 545 rpm, after evacuation, 6.5 l of demineralized water and 260 ml of a perfluoropolyoxyalkylene microemulsion were introduced: the latter was previously obtained by mixing:

- 56.4 ml of a perfluoropolyoxyalkylene, having an acid end group, of formula:



wherein $n/m = 10$, having average molecular weight of 600;

- 56.4 ml of a 30% by volume NH_4OH aqueous solution;
- 112.8 ml of demineralized water;
- 34.4 ml of Galden^(R) D02 of formula:



wherein $n/m = 20$, having average molecular weight of 450.

[0064] The autoclave was then heated up to 80°C and maintained at said temperature for the whole reaction duration. The autoclave was pressurized to the pressure of 0.56 bar with ethane and then to the pressure of 25 bar with a monomer mixture formed of 10% by moles of perfluoromethylvinylether (PMVE) and 90% by moles of tetrafluoroethylene (TFE).

[0065] 1.3 g of ammonium persulphate (APS) as initiator agent and at 66% of the monomer conversion 2.9 g of $\text{C}_6\text{F}_{12}\text{I}_2$ as chain transfer agent were then introduced in the autoclave.

[0066] During the reaction the pressure is maintained at 25 bar by continuously feeding the following monomer mixture: 3.5% by moles of PMVE and 96.5% of TFE.

[0067] After 29 minutes of reaction, the autoclave was cooled, degassed and discharged. The latex characteristics are reported in Table 3. Subsequently 4,941.8 ml (corresponding to 637.5 g of polymer) of the latex are introduced again in the 10 litre reactor to which 1,558 ml of demineralized water are added. The autoclave is then heated up to 90°C and maintained for one hour at said temperature in order to decompose all the residual initiator agent. Subsequently the temperature is decreased to 80°C and maintained constant for the whole duration of the polymerization. The following mixture of monomers was then fed:

perfluoromethylvinylether (PMVE)

60% by moles

tetrafluoroethylene (TFE)

40% by moles

so as to increase the pressure up to 25 bar.

- 0.32 g of ammonium persulphate (APS) as initiator agent;
- 22.26 g of 1,6-diiodoperfluorohexane ($\text{C}_6\text{F}_{12}\text{I}_2$) as chain transfer agent;
- 4.28 g of bis-olefin of formula $\text{CH}_2=\text{CH}(\text{CF}_2)_6\text{CH}=\text{CH}_2$; the addition was carried out in 20 portions, each of 0.214 g, starting from the polymerization beginning and for every 5% increase in the monomer conversion,

[0068] The 25 bar pressure was maintained constant for the whole duration of the polymerization by feeding a mixture formed of:

perfluoromethylvinylether (PMVE)

40% by moles

tetrafluoroethylene (TFE)

60% by moles

[0069] After 200 minutes of reaction corresponding to 2,550 g of elastomer produced, the autoclave was cooled and the latex discharged.

[0070] The latex is coagulated with an aluminum sulphate solution (6 g of $\text{Al}_2(\text{SO}_4)_3$ for each litre of latex) and dried at 80°C in an air-circulating oven for 10 hours. The obtained polymer was characterized as shown in Table 4.

EXAMPLE 6**a) Preparation of the semicrystalline fluoropolymer**

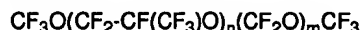
5 [0071] In a 10 l autoclave, equipped with a stirrer working at 545 rpm, after evacuation, 6.5 l of demineralized water and 260 ml of a perfluoropolyoxyalkylene microemulsion were introduced: the latter was previously obtained by mixing:

- 56.4 ml of a perfluoropolyoxyalkylene, having an acid end group, of formula:



wherein $n/m = 10$, having average molecular weight of 600;

- 56.4 ml of a 30% by volume NH_4OH aqueous solution;
- 112.8 ml of demineralized water;
- 15 - 34.4 ml of Galden^(R) D02 of formula:



wherein $n/m = 20$, having average molecular weight of 450.

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[0072] The autoclave was then heated up to 80°C and maintained at said temperature for the whole reaction duration. The autoclave was pressurized to the pressure of 0.56 bar with ethane and then to the pressure of 25 bar with a monomer mixture formed of 10% by moles of perfluoromethylvinylether (PMVE) and 90% by moles of tetrafluoroethylene (TFE).

25 [0073] 1.3 g of ammonium persulphate (APS) as initiator agent and at 66% of the monomer conversion 2.9 g of $\text{C}_6\text{F}_{12}\text{I}_2$ as chain transfer agent were then introduced in the autoclave.

[0074] During the reaction the pressure is maintained at 25 bar by continuously feeding the following monomer mixture: 3.5% by moles of PMVE and 96.5% of TFE.

[0075] After 29 minutes of reaction, the autoclave was cooled and the latex discharged. The latex properties are reported in Table 3.

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b) Preparation of the fluoroelastomer

[0076] The perfluoroelastomer latex was obtained as reported in Example 4b. The latex characteristics are reported in Table 3.

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c) Mixing of the latexes - Preparation of the final polymer

[0077] 581.4 ml of the latex obtained in Example 6a are mixed with 1187 ml of the Example 6b latex. After mixing, the latex is coagulated with an aluminum sulphate solution (6 g of $\text{Al}_2(\text{SO}_4)_3$ for each litre of latex) and dried at 80°C in an air-circulating oven for 10 hours. 500 g of polymer, characterized as shown in Table 4, were obtained.

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TABLE 1

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	Latex concentration (g/l)	Particle diameter (nm)	MFI ⁽¹⁾ ASTM D 1238	Mooney (1+10) ^{121°C} ASTM D 1646
Example 1a	126	13	29.8	-
Example 1b	280	78	-	27
Example 3	126	13	29.8	-

50

(1) MFI has been measured at 380°C with 3 Kg

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TABLE 2

EXAMPLE		Ex.1c	Ex.1D comp.	Ex.2	Ex.3
% by weight of plastomer		15	15	15	20
ML(1+10) ^{121°C} (ASTM D 1646)		51	-	51	31
Formulation:					
Elastomer	(phr)	100	100	100	100
TAIC	"	1.5	1.5	-	1.5
BO ⁽¹⁾	"	-	-	4	-
Luperco	"	2	2	1.5	2
ZnO	"	5	5	5	5
ODR (177°C,12'arc 3°) (ASTM D2084-81):					
ML	Lbf.in.	8	13	5	6
MH	"	118	140	83	126
Ts2	sec	45	51	84	46
T90	"	111	109	414	103
Molding In press at 180°C for 10 min:					
Sheet surface		smooth	rough	smooth	smooth
Mechanical properties after post cure at 200°C for 1 hour (ASTM D 412- 83):					
M100	Mpa	4.3	6.3	3.2	5.3
C.R.	"	19.2	18.7	19.9	18
A.R.	%	184	174	234	178
ShA Hardness	points	66	76	65	71
Thermal resistance at 290°C after 168 hours (ASTM D 573):					
ΔM100	%			+22	
ΔC.R.	"			+34	
ΔA.R.	"			-17	
ΔShA hardness	points			- 3	
Compression set on O-ring (ASTM D 395):					
200°C for 70 hours	(%)	35	broken	55	42

(2) Bisolefin of formula $\text{CH}_2=\text{CH}-(\text{CF}_2)_6-\text{CH}=\text{CH}_2$

TABLE 3

	Latex concentration (g/l)	Particle diameter (nm)	MFI ⁽¹⁾ ASTM D 1238	Mooney (1+10) ^{121°C} ASTM D 1646
Example 4a	196	66	57	-
Example 4b	358	54	-	15
Example 5	129	15	101	-
Example 6a	129	15	101	-
Example 6b	358	54	-	15

(1) MFI has been measured at 372°C with 5 Kg

TABLE 4

EXAMPLE		Ex.4c	Ex.5	Ex.6c
% by weight of plastomer		15	20	15
ML(1+10) ^{121°C} (ASTM D 1646)		29	36	44
Formulation:				
Elastomer	(phr)	100	100	100
TAIC	"	1.5	1.5	1.5
Luperco	"	2	2	2
ZnO	"	5	5	5
ODR (177°C, 12'arc 3°) (ASTM D2084-81):				
ML	Lbf.in.	8	9	14
MH	"	135	117	135
Ts2	sec	51	54	52
T90	"	109	100	114
Molding in press at 180°C for 10 min:				
Sheet surface		smooth	smooth	smooth
Mechanical properties after post cure at 200°C for 1 h (ASTM D 412-83):				
M100	Mpa	8.3	6.3	8.9
C.R.	"	20.1	20.3	19.6
A.R.	%	171	184	164
ShA hardness	points	76	75	76
Compression set on O-ring (ASTM D 395):				
200°C for 70 hours	(%)	29	38	40
230°C for 70 hours	(%)	54	-	-

Claims

1. Fluoropolymers comprising a fluoroelastomer matrix incorporating therein particles of a semi-crystalline fluoropolymer latex containing iodine and/or bromine and formed of tetrafluoroethylene (TFE) homopolymers, or TFE copolymers with one or more monomers containing at least one unsaturation of ethylene type in amounts ranging from 0.01% to 10% by moles, preferably from 0.05% to 5% by moles, wherein the average particle sizes of the semicrystalline fluoropolymer latex range from 10 to 100 nm for at least 60% by weight of the semicrystalline fluoropolymer.
2. Fluoropolymers according to claim 1 wherein the latex particle sizes of the semicrystalline fluoropolymer range from 10 to 60 nm.
3. Fluoropolymers according to claims 1-2 obtainable by mixing the semicrystalline fluoropolymer latex with the fluoroelastomer latex and subsequent coagulation.
4. Fluoropolymers according to claims 1-2 obtainable by polymerizing in a first step the semicrystalline fluoropolymer and in a second step the fluoroelastomer.
5. Fluoropolymers according to claims 1-4 wherein the semicrystalline fluoropolymer amount inside the fluoroelastomer matrix is in the range 2%-40% by weight on the total of the polymer mixture.
6. Fluoropolymers according to claim 5 wherein the semicrystalline fluoropolymer amount inside the fluoroelastomer matrix is in the range 5-30% by weight on the total of the polymer mixture.
7. Fluoropolymers according to claims 1-6 wherein the semicrystalline fluoropolymers contain in end position of the macromolecules and/or in the chain iodine and/or bromine atoms.
8. Fluoropolymers according to claims 1-7 wherein the iodine and/or bromine atoms derive from brominated and/or iodinated comonomers selected from: bromo- and/or iodo-olefins having from 2 to 10 carbon atoms, iodo- and/or bromo-fluoroalkylvinylethers; the amount of said comonomers being in the range 0.05%-2% by moles of the other base monomer units.
9. Fluoropolymers according to claims 1-8 wherein the iodine and/or bromine atoms derive from iodinated and/or brominated chain transfer agents selected from:
 - compounds of formula $R_f(I)_x(Br)_y$, wherein R_f is a (per)fluoroalkyl or a (per)fluorochloroalkyl having from 1 to 8 carbon atoms, while x and y are integers between 0 and 2, with $1 \leq x+y \leq 2$;
 - alkaline or earth-alkaline metal iodides and/or bromides;
 - tri-iodinated compounds deriving from triazines; the content by weight of iodine and/or bromine in the semicrystalline fluoropolymer being in the range 0.01-5% by weight.
10. Fluoropolymers according to claims 1-9 wherein the semicrystalline polymer is based on PTFE modified with comonomers with ethylene unsaturation both of hydrogenated and fluorinated type.
11. Fluoropolymers according to claim 10 wherein the hydrogenated comonomers are selected from ethylene, propylene, methylmethacrylate, methacrylic acid, butylacrylate, hydroxyethylhexylacrylate, styrene.
12. Fluoropolymers according to claim 10, wherein the fluorinated comonomers are selected from:
 - perfluoroolefins C_3-C_8 , such as hexafluoropropene (HFP), hexafluoroisobutene;
 - hydrogenated fluoroolefins C_2-C_8 , such as vinyl fluoride (VF), vinylidene fluoride (VDF), trifluoroethylene, perfluoroalkylethylene $CH_2=CH-R_f$, wherein R_f is a perfluoroalkyl C_1-C_6 ;
 - chloro- and/or bromo- and/or iodo-fluoroolefins C_2-C_8 , such as chlorotrifluoroethylene (CTFE);
 - (per)fluoroalkylvinylethers (PAVE) $CF_2=CFOR_f$, wherein R_f is a (per)fluoroalkyl C_1-C_6 , for example CF_3 , C_2F_5 , C_3F_7 ;
 - (per)fluoro-oxyalkylvinylethers $CF_2=CFOX$, wherein X is: an alkyl C_1-C_{12} , or an oxyalkyl C_1-C_{12} , or a (per)fluoro-oxyalkyl C_1-C_{12} having one or more ether groups, for example perfluoro-2-propoxy-propyl; fluorodioxoles.

13. Fluoropolymers according to claim 12 wherein the preferred comonomers are perfluoromethyl-, ethyl-, propylvinylether and perfluorodioxoles.

14. Fluoropolymers according to claims 1-13 wherein the fluoroelastomer is selected from the following classes:

(1) vinylidene fluoride (VDF)-based copolymers, wherein VDF is copolymerized with at least one comonomer selected from the following ones: perfluoroolefins C₂-C₈, such as tetrafluoroethylene (TFE), hexafluoropropene (HFP); chloro- and/or bromo- and/or iodo-fluoroolefins C₂-C₈, such as chlorotrifluoroethylene (CTFE) and bromotrifluoroethylene; (per)fluoroalkylvinylethers (PAVE) CF₂=CFOR_f, wherein R_f is a (per)fluoroalkyl C₁-C₆, for example trifluoromethyl, bromodifluoromethyl, pentafluoropropyl; perfluoro-oxyalkylvinylethers CF₂=CFOX, wherein X is a perfluoro-oxyalkyl C₁-C₁₂ having one or more ether groups, for example perfluoro-2-propoxypropyl; non fluorinated olefins (OI) C₂-C₈, for example ethylene and propylene;

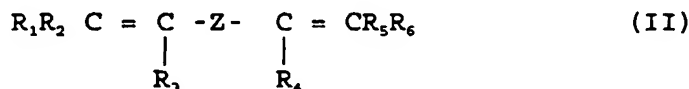
(2) tetrafluoroethylene (TFE)-based copolymers, wherein TFE is copolymerized with at least one comonomer selected from the following:

(per)fluoroalkylvinylethers (PAVE) CF₂=CFOR_f, wherein R_f is as above defined; perfluoro-oxyalkylvinylethers CF₂=CFOX, wherein X is as above defined; fluoroolefins C₂-C₈ containing hydrogen and/or chlorine and/or bromine and/or iodine atoms; non fluorinated olefins (OI) C₂-C₈; perfluorovinylethers containing cyano groups.

15. Fluoropolymers according to claim 14 wherein the fluoroelastomer is selected from the following compositions expressed by moles:

(a) vinylidene fluoride (VDF) 45-85%, hexa-fluoropropene (HFP) 15-45%, tetrafluoroethylene (TFE) 0-30%;
 (b) vinylidene fluoride (VDF) 50-80%, perfluoroalkylvinylether (PAVE) 5-50%, tetrafluoroethylene (TFE) 0-20%;
 (c) vinylidene fluoride (VDF) 20-30%, non fluorinated olefins (OI) C₂-C₈ 10-30%, hexafluoropropene (HFP) and/or perfluoroalkylvinylether (PAVE) 18-27%, tetrafluoroethylene (TFE) 10-30%;
 (d) tetrafluoroethylene (TFE) 50-80%, perfluoroalkylvinylether (PAVE) 20-50%;
 (e) tetrafluoroethylene (TFE) 45-65%, non fluorinated olefins (OI) C₂-C₈ 20-55%, vinylidene fluoride 0-30%;
 (f) tetrafluoroethylene (TFE) 32-60% by moles, non fluorinated olefins (OI) C₂-C₈ 10-40%, perfluoroalkylvinylether (PAVE) 20-40%;
 (g) tetrafluoroethylene (TFE) 33-75%, perfluoroalkylvinylether (PAVE) 15-45%, vinylidene fluoride (VDF) 5-30%.

16. Fluoropolymers according to claims 1-15 wherein the fluoroelastomer comprises also monomer units deriving from a bis-olefin having general formula:



wherein:

R₁, R₂, R₃, R₄, R₅, R₆, equal to or different from each other, are H or alkyls C₁-C₅;
 Z is a linear or branched, alkylene or cycloalkylene C₁-C₁₈ radical, optionally containing oxygen atoms, preferably at least partially fluorinated, or a (per)fluoropolyoxyalkylene radical.

17. Fluoropolymers according to claim 16 wherein the unit amount in the chain deriving from the bis-olefin is in the range 0.01-1.0% by moles of the other monomer units forming the fluoroelastomer base structure.

18. Fluoropolymers according to claims 1-17 wherein the fluoroelastomers are cured by peroxidic route.

19. Fluoropolymers according to claims 1-17 wherein the fluoroelastomers when they contain cyano groups are cured by tin organic compounds and/or di-aromatic aminic compounds.

20. Fluoropolymers according to claim 19 wherein the fluoroelastomers are cured by tin organic compounds and/or

diaromatic aminic compounds and optionally by peroxidic route if in the polymer chain iodine and/or bromine atoms are present.

21. Use of fluoropolymers according to claims 1-20 for the preparation of sealing manufactured articles.

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EUROPEAN SEARCH REPORT

Application Number
EP 00 10 3032

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	EP 0 127 407 A (DU PONT) 5 December 1984 (1984-12-05) * abstract; claims 1-25 * * page 3, line 17-30 * * page 4, line 1 - page 5, line 29 * * page 6, line 5 - page 7, line 8 * * page 8, line 20-25 * * page 9, line 1-25 *	1-21	C08L27/18 /(C08L27/18, 27:12)
D,A	US 4 035 565 A (APOTHEKER DAVID ET AL) 12 July 1977 (1977-07-12) * abstract; claims 1-12 * * column 1, line 5-20 * * column 2, line 5 - column 3, line 30 * * column 6, line 19-46 * * column 7, line 5-20 *	1-21	
A	US 5 153 272 A (LAGOSTINA ATTILIO ET AL) 6 October 1992 (1992-10-06) * abstract; claims 1-8 * * column 1, line 5-10 * * column 2, line 3-59 *	1-21	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C08L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 3 May 2000	Examiner Bergmans, K
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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 10 3032

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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03-05-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0127407 A	05-12-1984	US 4469846 A	04-09-1984
		BR 8402359 A	26-12-1984
		CA 1210179 A	19-08-1986
		DE 3480793 D	25-01-1990
		JP 59232109 A	26-12-1984
US 4035565 A	12-07-1977	AU 1239876 A	13-10-1977
		BE 840099 A	27-09-1976
		CA 1076298 A	22-04-1980
		CA 1094247 A	20-01-1981
		DE 2612360 A	30-09-1976
		DE 2659972 C	11-05-1983
		DK 135176 A,B,	28-09-1976
		DK 571777 A,B,	21-12-1977
		FR 2305462 A	22-10-1976
		GB 1528341 A	11-10-1978
		GB 1528342 A	11-10-1978
		IE 42664 B	24-09-1980
		IE 42665 B	24-09-1980
		IT 1061505 B	19-04-1983
		JP 925455 C	22-09-1978
		JP 51129481 A	11-11-1976
		JP 53004115 B	14-02-1978
		JP 967146 C	26-07-1979
		JP 52081360 A	07-07-1977
		JP 54001585 B	26-01-1979
		LU 74645 A	28-01-1977
		NL 7603217 A,B	29-09-1976
		NL 7810787 A,B	30-03-1979
		SE 410001 B	17-09-1979
		SU 747434 A	23-07-1980
US 5153272 A	06-10-1992	IT 1231174 B	22-11-1991
		AT 115164 T	15-12-1994
		AU 630480 B	29-10-1992
		AU 5973590 A	24-01-1991
		CA 2021639 A	25-01-1991
		CN 1049019 A,B	06-02-1991
		DE 69014746 D	19-01-1995
		DE 69014746 T	27-04-1995
		EP 0410351 A	30-01-1991
		ES 2066055 T	01-03-1995
		JP 3059057 A	14-03-1991
		RU 2068425 C	27-10-1996
		ZA 9005741 A	29-05-1991

EPO FORM P0469

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82